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AN XPS EXAMINATION OF SIX ORE POWDERS FOLLOWING VARIOUS TREATMENTS

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6 Samples submitted for analysis by Dr. G. Jean

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ABSTRACT

The surface composition and surface chemistry of six ore powders, submitted by the "Separation and Characterization Section" of HPRL were determined by X-ray photoelectron spectroscopy (XPS). Two ores, pendlandite and a complex Nb silicate had not been treated prior to analysis. The remaining four ores had been pre-reacted as follows: pyrite in HCℓ solution, pyrrhotite in bromine, sphalerite and pyrrhotite in mercuric chloride solution. Except for the sphalerite sample, much of the original near surface sulphide sulphur had been oxidized to sulphate. Nil or trace chlorine and mercury species were detected on the treated sulphide ore surfaces. However, a large bromine enrichment (≈ 40 wt.%) was measured on the pyrrhotite ore surface.

RÉSUMÉ

La surface de six minerais, provenant de la section "Séparation et caractérisation", a été analysée par la spectroscopie photoélectronique à rayon-X (XPS).

Deux de ces minerais (pendlandite et un complexe Nb-silicate) n'avaient pas été chimiquement traités. Les quatre autres avaient été traités comme suit: pyrite avec une solution de HCℓ, pyrrhotite avec du brome pur, sphalerite et pyrrhotite avec une solution de $HgCℓ_2$.

A l'exception de la sphalérite, le soufre présent en surface avait été oxidé en sulfate. Seulement des traces de chlore et de mercure furent détectées à la surface de ces minerais sulfureux. La pyrrhotite traitée au brome avait en surface une large concentration de brome (40% poids).

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EXPERIMENTAL PROCEDURES AND INSTRUMENTATION

A. SAMPLE PREPARATION

Each specimen was pressed into a KBr type pellet (10 mm x 2 mm) using an IR die and hydraulic press, then dried at 100°C in an oven overnight. This pellet was then mounted on the specimen insert probe and evacuated to $\approx 10^{-6}$ torr in the preparation/pumpdown chamber.

B. INSTRUMENTATION

A combination x-ray photoelectron (XPS) and Auger electron spectrometer (AES) manufactured by Physical Electronics Division, Perkin-Elmer Corporation (PHI-548E) having depth profiling capability (Ar^+ 5KeV ion gun Model PHI-4303), specimen introduction and transfer fore-chamber (PHI-2100) and multiple-technique analytical computer system (MACS) was employed for this investigation. The base pressure of this instrument is $\approx 2 \times 10^{-10}$ torr (ultra-high vacuum, UHV).

X-ray photoelectron spectroscopy (XPS) also called electron spectroscopy for chemical analysis (ESCA) and Auger electron spectroscopy (AES) are highly surface sensitive, direct and in many cases non-destructive. Both XPS and AES readily provide qualitative information (which elements are present), by probing the outermost 1-5 nm region of a sample's surface. When calibration techniques (element and instrument sensitivity factors) are used, semi-quantitative and in some cases quantitative surface composition data is possible.

All elements, except hydrogen and helium can be detected with an ultimate sensitivity approaching 10^{-9} gm cm^{-2} of surface. Usually it is possible to confirm chemical environment (oxidation state, co-ordination number) of a surface sited element from XPS binding energies (chemical shift information).

Extensive reviews of XPS (1-5) theory and use are available. Details of the specifications and features of the PHI multi-technique XPS/AES instrument utilized in this study are available (6).

Each sample was placed on an introduction sample holder, mounted on the specimen insert probe and evacuated to $\approx 10^{-7}$ torr in the preparation forechamber. XPS analyses were performed at $\approx 10^{-9}$ torr in the analytical chamber using a dual Al/Mg anode equipped x-ray gun operating at 300 W (15 KeV x 20 mA) in the Mg k_δ mode. The resulting x-rays of energy $\approx$1254 eV were directed onto an $\approx$ 5 mm^2 area of the sample.

The quantity of electrons photoejected by x-rays (XPS) and their kinetic energies are monitored using a high resolution double pass cylindrical mirror electron energy analyzer (CMA) with a coaxially mounted electron gun and associated electronics. The entire analytical operation is computer controlled. A spectrum of peak intensity (electron counts) vs. binding energy is then plotted. Samples are normally examined using two XPS scanning modes:

(a) initial "surveying" for determining all elements present; and

(b) "multiplexing" specific regions of the survey at greater resolution for quantitative and/or chemical structure information

The XPS "survey technique" can identify elements present down to the minor element level by sweeping the binding energy scale (0 → 1254 eV) in 1 eV/100 microsecond increments using a CMA pass energy of 100 eV. Spectrum acquisition times for acceptable S/N level spectra is usually 15 minutes. For the "multiplex technique", ultimate resolution is achieved at lower pass energies, typically 25 or 50 eV and binding energy windows of either 10, 20 or 40 eV depending on the complexity of an individual photoelectron line envelope and on the proximity of one peak to another. Acquisition times for multiplex spectra vary greatly depending on the element's surface concentration. The time required to give an acceptable S/N multiplex spectrum for elements present at the major and minor level are typically 5 minutes and 15 minutes respectively.

The carbon (C 1s) signal is used to determine the degree of specimen charging; an electron flood gun (specimen neutralizer) is used to greatly reduce charging of insulators and hence eliminate identification problems caused by differential charging (ghost) peaks. Thus all XPS photoelectron lines are referenced to the accepted hydrocarbon C 1s binding energy of 284.6 eV. Gold foil is used to calibrate the energy scale of the spectrometer (Au $4f_{7/2}$ = 83.8 eV).

DISCUSSION

A. XPS RESULTS

1. Pyrite treated in hydrogen chloride:

The surface composition of this acid exposed sample shown in Table 1 was determined from the XPS spectrum (Figure 1). The surface of the pyrite contained 2 species of sulphur (Figure 2) ≈ 16 At.% sulphide (SII) and ≈ 4 At.% sulphate (SVI). The sulphate content was attributable to air exposure during grinding and to the acid treatment process. However, only trace chloride was detected on the surface (≈ 0.2 At.%). The measured iron content (≈ 6 At.%) was mostly present as FeII (a peak binding energy of ≈ 707 eV) and assigned to FeS_2. There was a significant content of silicon measured (≈ 10 At.%) which is most probably sited as the silica and silicate gangue rock matrix associated with the pyrite ore. Note the oxygen content measured directly (≈ 36 At.%) agrees very well with the oxygen values required for chemical balance of the sulphate (4 At.% S(VI)) and silica (10 At.% Si(II)).

2. Pyrrhotite treated in Bromine:

The XPS survey spectrum is shown in Figure 4 and the corresponding surface composition in Table 2. The bromine content is very large (≈ 12 At.%) while the sulphur and iron levels are much lower than expected for FeS ore. Thus the exposure to bromine has greatly altered the surface. No silica or silicate matrix minerals are detected.

3. Pentlandite $(Fe, Ni)_9S_8$

The results of this XPS examination are shown in Table 3 and Figure 4a,b. The XPS survey spectrum indicate the presence of iron, nickel, copper and sulphur; elements associated with the ore. In addition, smaller amounts of Si, Al, and Cl (gangue rock constituents) are detected. The sulphur content is equally split between sulphate (≈ 4 At.%) and sulphide (≈ 4 At.%) species. The large oxygen content indicates the pentlandite ore has been significantly oxidized. The high Al/Si ratio would indicate the presence of Al rich minerals such as gibbsite rather than Al-silicates. The copper detected is probably an ore constituent, (cholcopyrite etc), however the specimen was clamped to the XPS holder using a copper clip which may have been in the X-ray beam path.

4. Sphalerite exposed to $HgCl_2$

The surface chemical composition of this sample is shown in Table 4, Figure 5. The results indicate that little or nil $HgCl_2$ is present at the surface. The Zn and S measured are 19.1 and 19.9 At.% respectively. All of the sulphur detected is the sulphide species S(II). Thus these results infer that the sample is essentually pure ZnS with some Fe and Cu present probably as oxidized sulphide minerals (pyrite, chalcopyrite etc.). No silica or silicate gangue minerals were detected.

5. Pyrrhotite exposed to $HgCl_2$

The surface chemical composition of this specimen (Table 5) were determined from the XPS survey peak intensities (Figure 6). The major constituents are O, S, Fe and carbon. No Hg or Cl species were detected and only small amounts of Cu, Ni, Si and Al. The Cu and Ni are either from the XPS holder or the sample, however the Si and Al are present as Al-silicate mineral constituents. The surface of the pyrrhotite has been largely oxidized based on the large sulphate sulphur component (SVI) measured. The surface iron is mostly in the oxide, or oxy-hydroxide form with little of the underlying sulphide iron detectable. Since the escape depth for sulphur 2p electrons is greater than iron 2p electrons, the underlying sulphide sulphur is more easily seen. The oxidized layer is therefore only ≈ 10-50 Å thick, if greater no sulphide sulphur electrons would be monitored.

6. Ta-Nb rich ore

The XPS survey spectrum is shown in Figure 7. The surface chemical composition of this ore as determined from this survey is reported in Table 6. The major components of this ore are silicon and oxygen. The silicon 2p position can be assigned as originating from a complex silicate mineral phase (SiO_3). The oxygen content (≈ 57 At.%) measured directly agrees well with this assignment (silicon content of ≈ 18 At.%). Small amounts of Fe, Nb and possibly Ta as well as Ca and P (as oxides) were present. No sulphur was detected in this sample. Phosphorous and iron are common elements in alkaline igneous rocks containg Nb and Ta. Ta substitutes easily for Nb in minerals such as columbite ($FeO \cdot Nb_2O_5$) and pyrochlore (complex niobate). Note, the Ta content determined is questionable because the O 2s peak closely overlaps with the Ta 4f region at ≈ 25 eV binding energy. The survey spectrum (Figure 7a) indicates 2 peaks at a binding energy of ≈ 291 eV and ≈ 285 eV. The 291 eV peak is assigned to hydrocarbon species with the sample charging ≈ 7 eV. Other peak positions confirm this 7 eV charge. The 285 eV peak cannot be positively identified, however it may be a non-charging carbon species such as graphite or a metal carbide. Na and K usually major components of alkaline igneous rocks were not present. The elements chlorine and lanthanum were also detected but at small levels.

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TABLE I

PYRITE DISC. TREATED IN HCL

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
C	28.5	15.9		
O	36.0	28.8		
Si	10.2	13.3		- 60% silicate + 40% oxide
Fe	5.8	15.1		- mostly FeS_2
S	19.5	29.0		- 85% S^{2-} and 15% S^{6+}
Ni	Trace	Trace		- possibly sample probe contamination.
Cl	Nil	Nil		

TABLE 2

PYRRHOTITE DISC. TREATED IN BROMINE

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
C	56.6	28.0		No silica or silicate matrix minerals detected.
O	22.6	14.9		
Fe	5.6	12.9		
S	3.1	4.3		
Br	12.1	39.9		- $FeBr_3$
Ni	Trace	Trace		- possibly sample probe contamination.

TABLE 3

PENTLANDITE($(Fe, Ni)_9S_8$) DISC.

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
C	35.3	22.0		
O	43.4	36.0		
Fe	4.4	12.8		
S	8.4	14.0		- 50% S^{2-} and 50% S^{6+}
Cu	0.8	2.6		- possibly contamination from the sample clips and the Ni alloy probe.
Ni	0.9	2.7		
Si	1.9	2.8		
Al	4.1	5.7		- High Al/Si ratio indicates Al rich minerals (ie: gibbsite) rather than Al-silicates.
Cl	0.8	1.5		

TABLE 4

SPHALERITE (ZnS) DISC. TREATED IN $HgCl_2$

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
C	30.6	12.5		
O	25.6	14.0		
Fe	3.8	7.2		
S	19.9	21.7		- 100% S^{2-}
Cu	0.9	2.0		Fe and Cu as oxidized sulphided minerals.
Zn	19.1	42.6		
Cl	Trace	Trace		No silica or silicate gangue minerals detected.
Hg	Trace to Nil	Trace to Nil		

TABLE 5

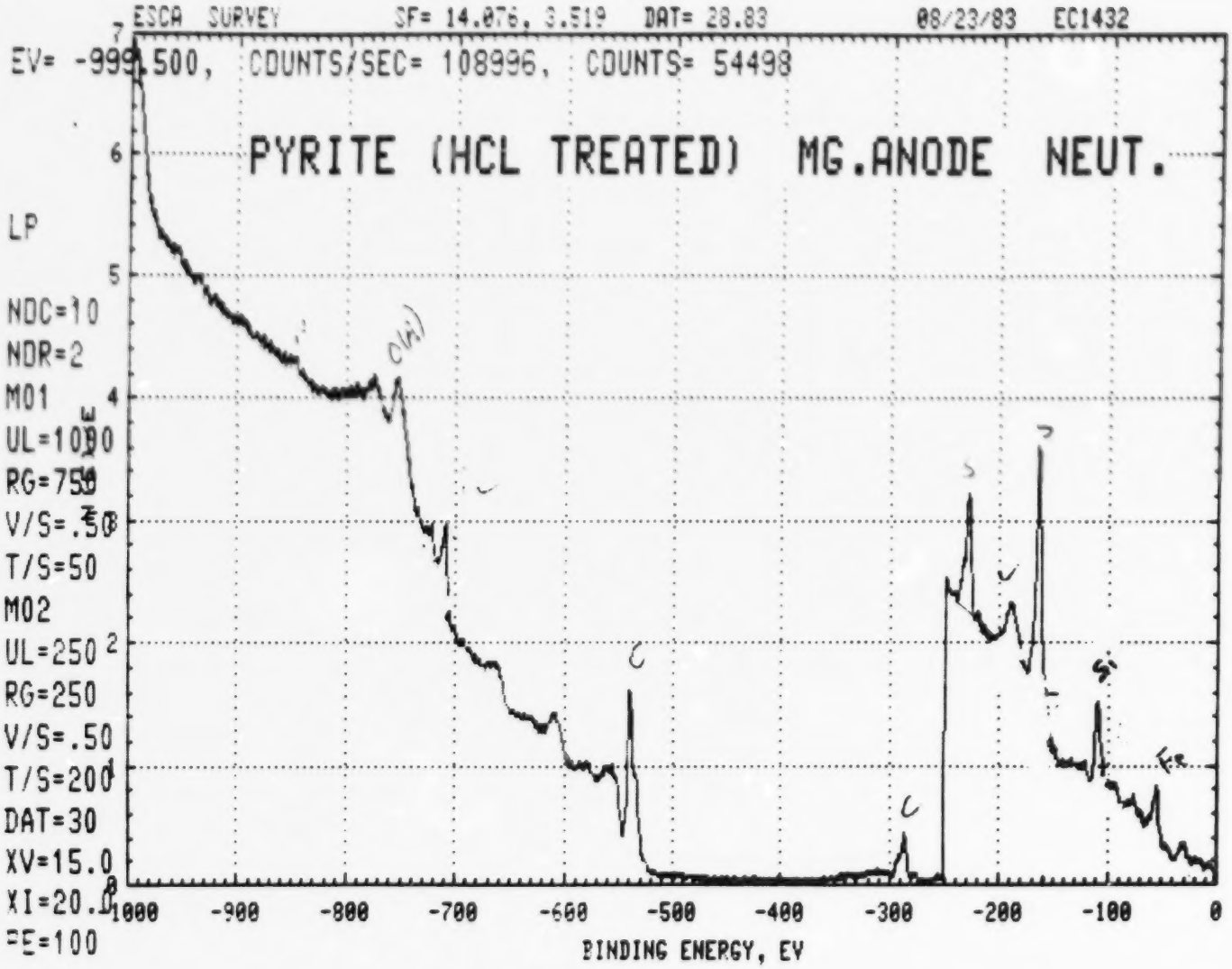
PYRRHOTITE DISC. TREATED IN $HgCl_2$

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
C	26.0	14.9		
O	49.6	37.8		
Fe	8.9	23.7		- oxide or oxy-hydroxide
S	8.4	12.8		- 50% S^{2-} and 50% S^{6+}
Cu	0.3	0.9		- Possibly contamination from Cu clips and Ni sample probe.
Ni	0.8	2.2		
Si	3.4	4.5		
Al	2.4	3.1		- Al-silicate mineral constituents
Hg	Nil	Nil		
Cl	Nil	Nil		

TABLE 6

Ta-Nb RICH ORE DISC.

Element	XPS		Bulk (Wt.%) (±5%)	Remarks
	At. % (±10%)	Wt. %		
C	19.7	12.3		- mostly hydrocarbon contamination
O	54.7	45.6		- all associated with Si.
Fe	1.1	3.2		
Si	20.5	29.9		- $(SiO_3)_n$
Nb	0.27	1.3		- Nb^{5+}
Ta	0.10	0.9		
Ca	0.5	1.0		- Ca^{2+}
P	1.5	2.4		
La	0.1	0.7		
Cl	1.4	2.6		- inorganic compound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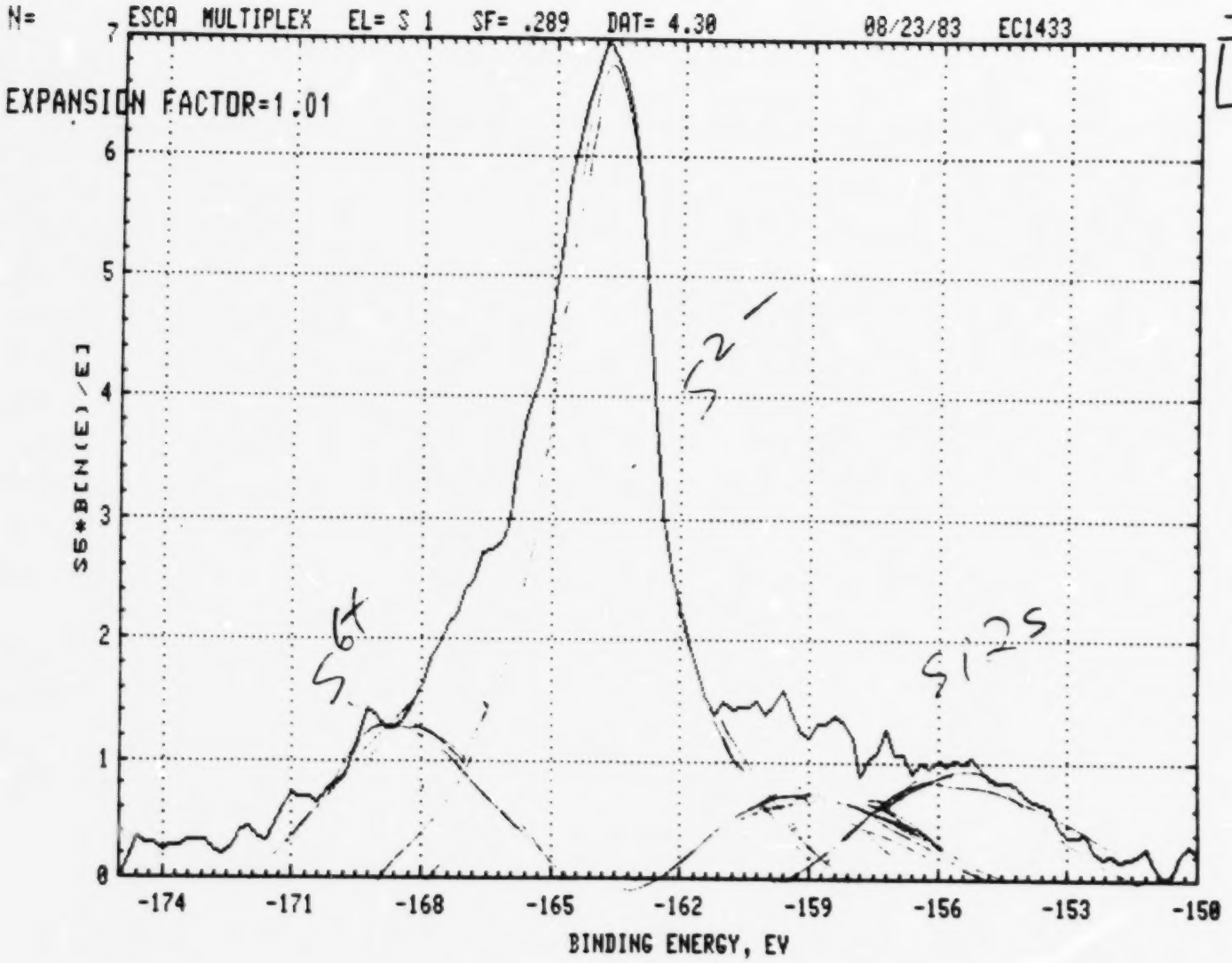
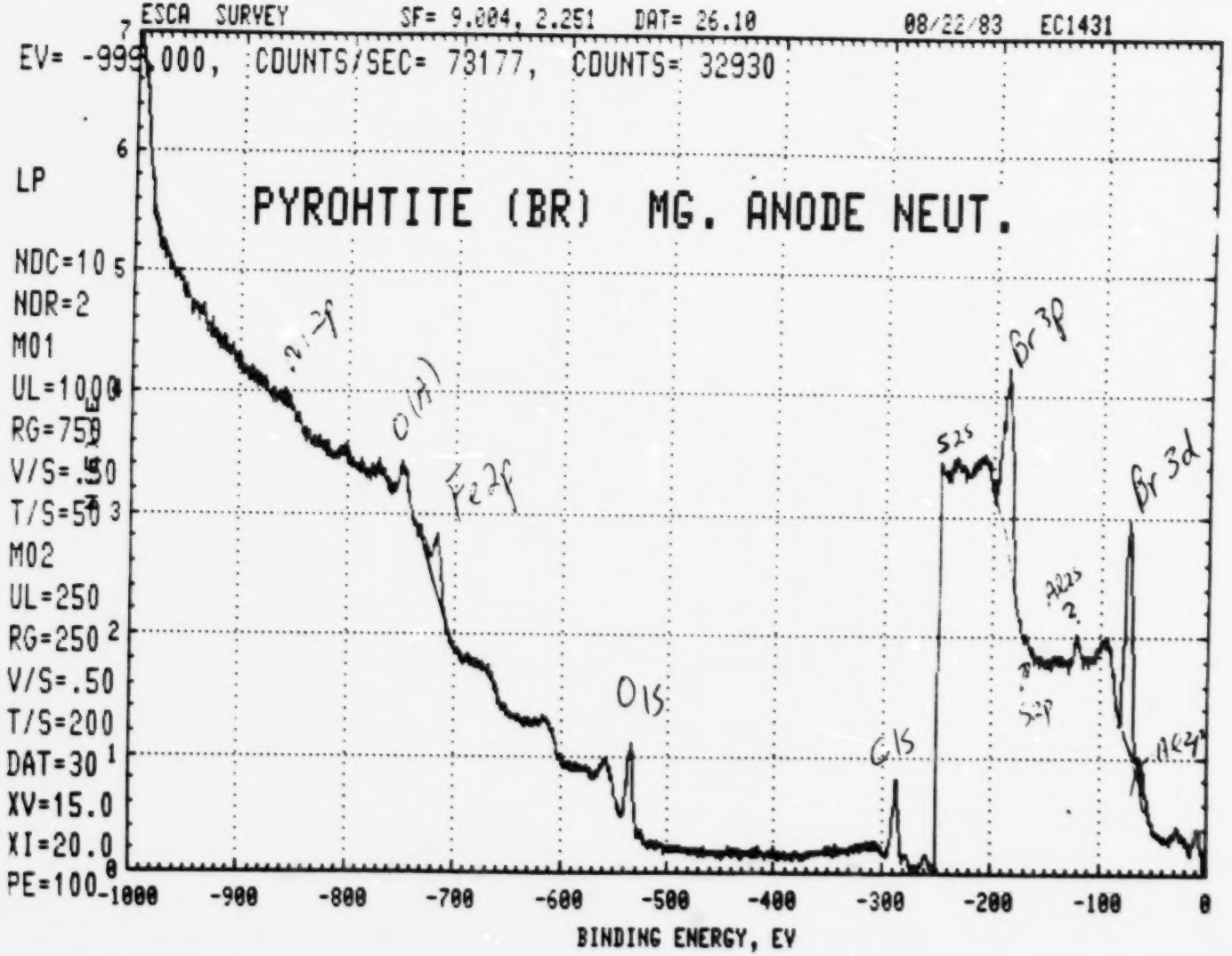
NDR=2
M01
UL=1000
RG=750
V/S=.50
T/S=50
M02
UL=250
RG=250
V/S=.50
T/S=200
DAT=30
XV=15.0
XI=20.0
PE=100
7
6
5
4
3
2
1
0
-1000 -900 -800 -700 -600 -500 -400 -300 -200 -100 0
BINDING ENERGY, EV
O(2s)
C
O
Si
Fe

Figure 1

163.8eV
−1.4
162.4eV

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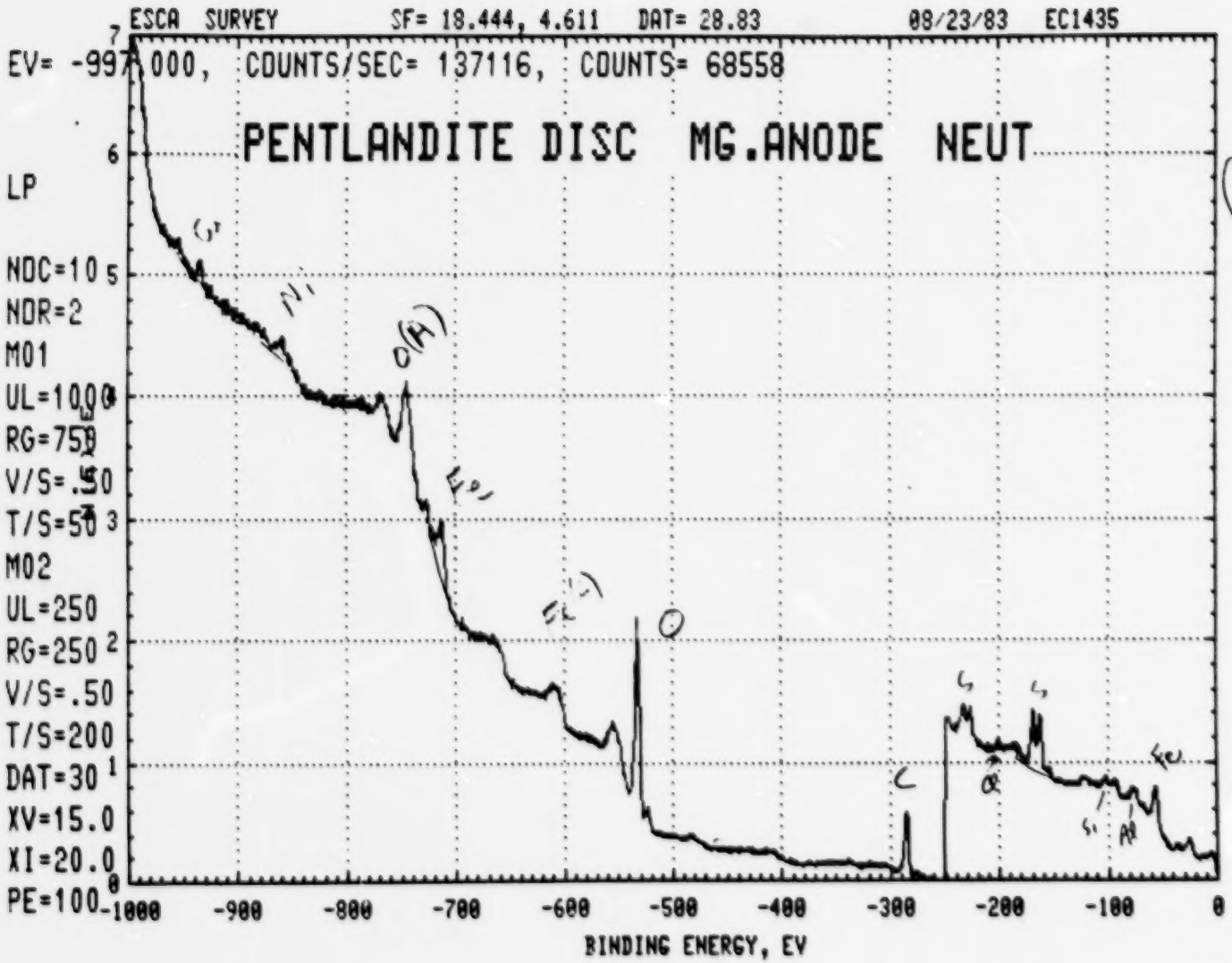
NDR=2
M01
UL=1000
RG=750
V/S=.50
T/S=50
M02
UL=250
RG=250
V/S=.50
T/S=200
DAT=30
XV=15.0
XI=20.0
PE=100
7
6
5
4
3
2
1
0
-1000
-900
-800
-700
-600
-500
-400
-300
-200
-100
0
BINDING ENERGY, EV
Fe 2p
O 1s
C 1s
S 2s
Br 3p
Br 3d

Figure 3

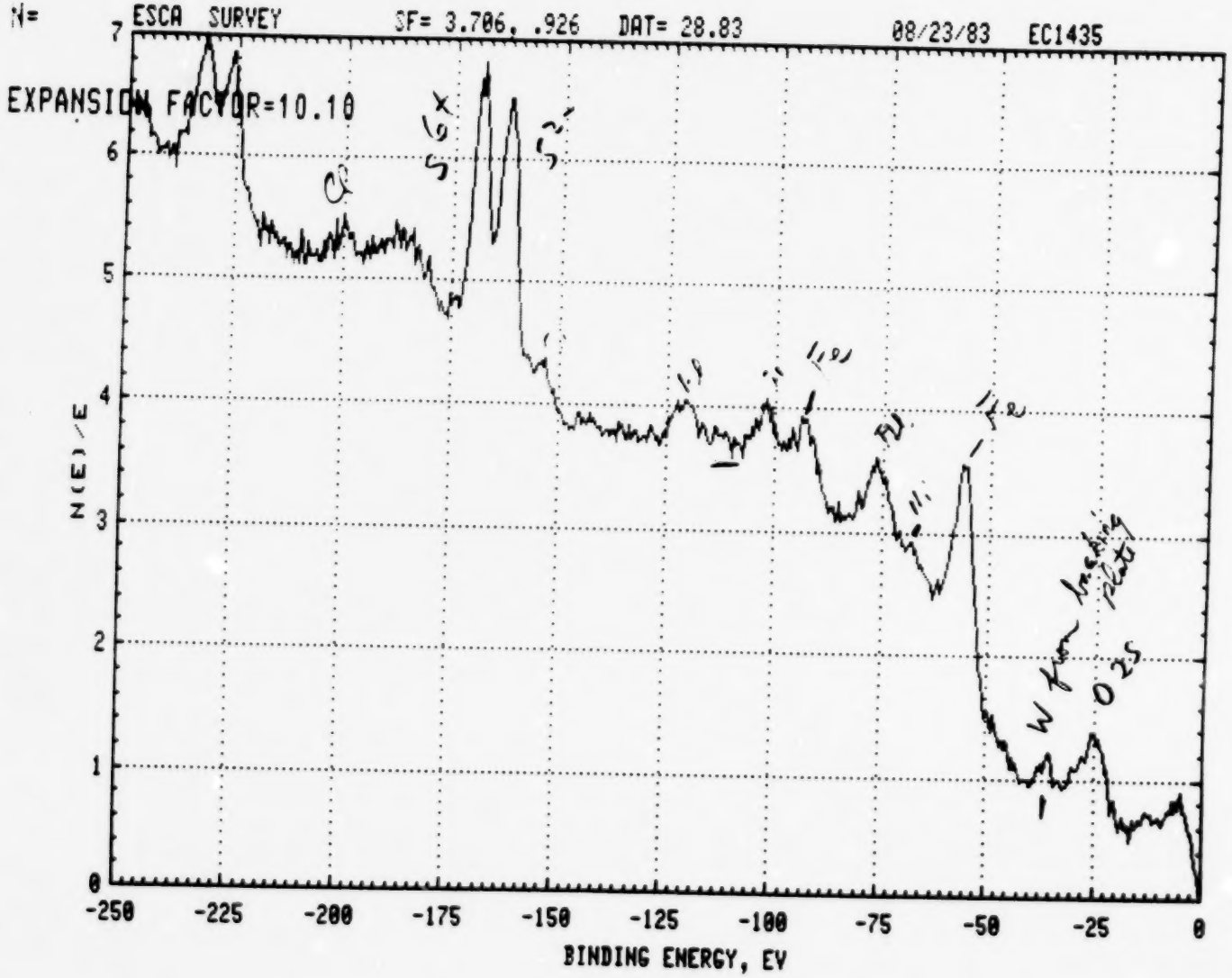


$(Fe,Ni)_9S_8$

+ Al, Si oxides

+ Cu present (clips?)

Figure 2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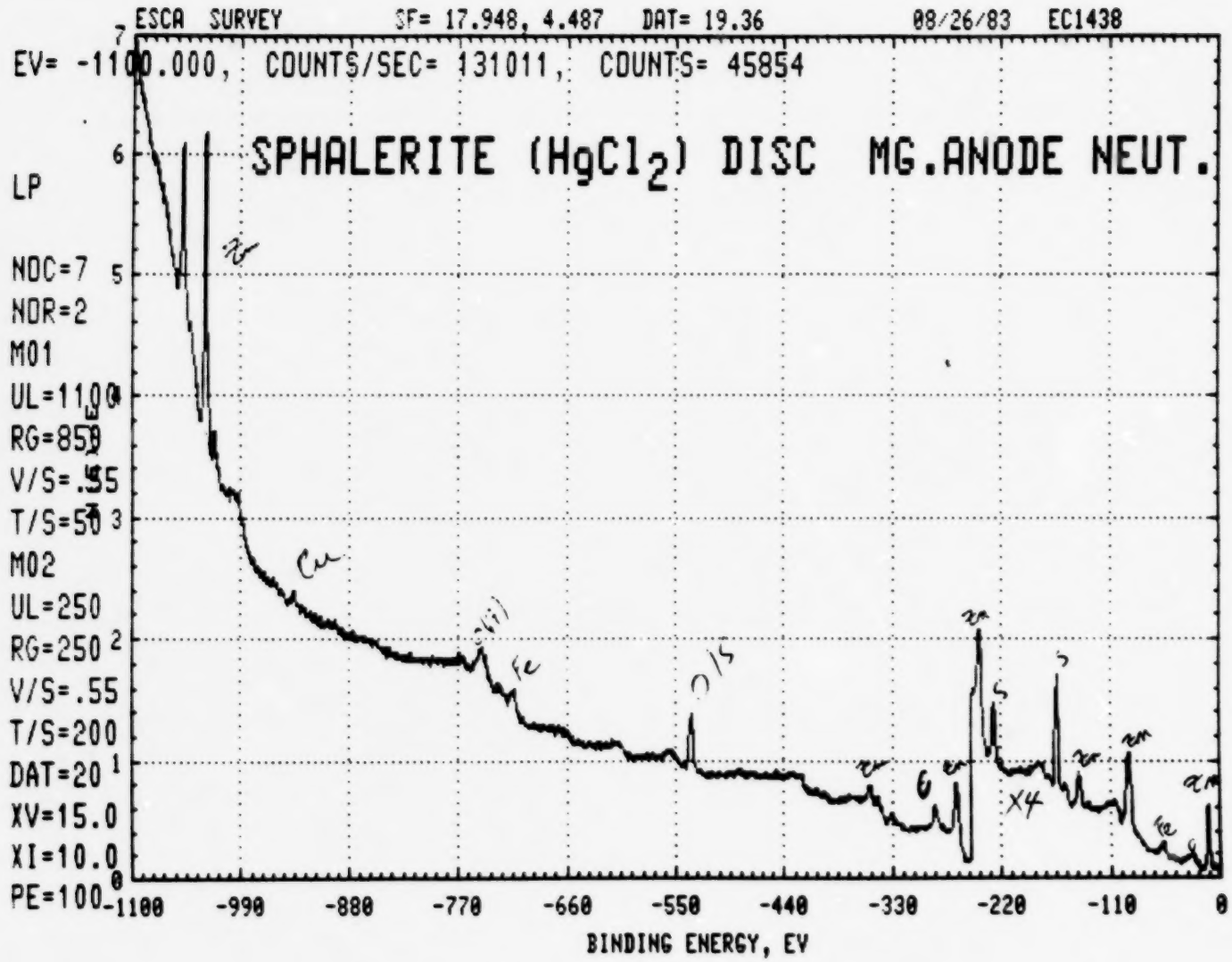
N(E)/E
BINDING ENERGY, EV
-250
-225
-200
-175
-150
-125
-100
-75
-50
-25
0
0
1
2
3
4
5
6
7

Figure 4b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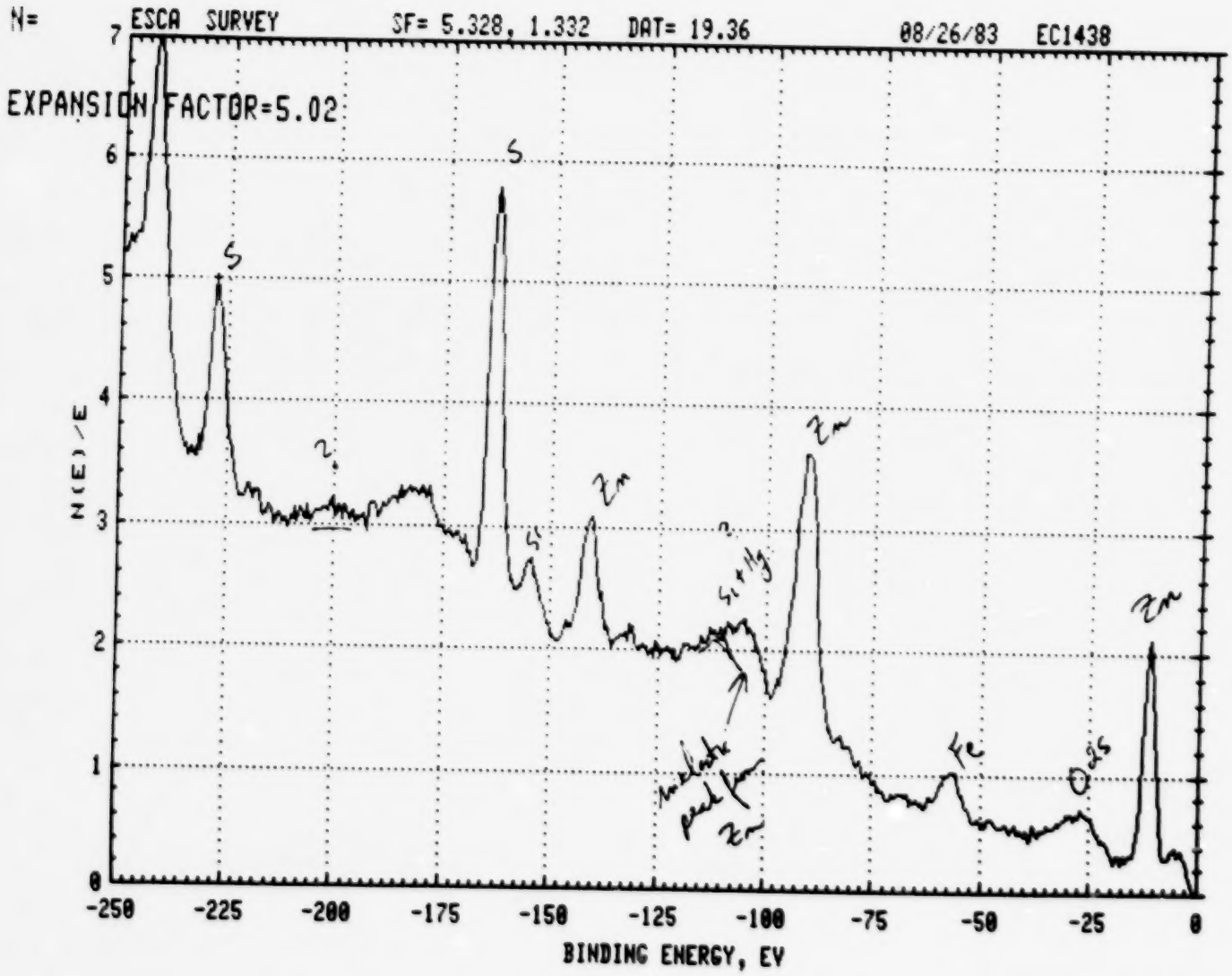
LP
NOC=7
NOR=2
M01
UL=1100
RG=850
V/S=.55
T/S=50
M02
UL=250
RG=250
V/S=.55
T/S=200
DAT=20
XV=15.0
XI=10.0
PE=100
7
6
5
4
3
2
1
0
-1100
-990
-880
-770
-660
-550
-440
-330
-220
-110
0
BINDING ENERGY, EV

Figure 5a


N=
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SF= 5.328, 1.332
DAT= 19.36
08/26/83
EC1438
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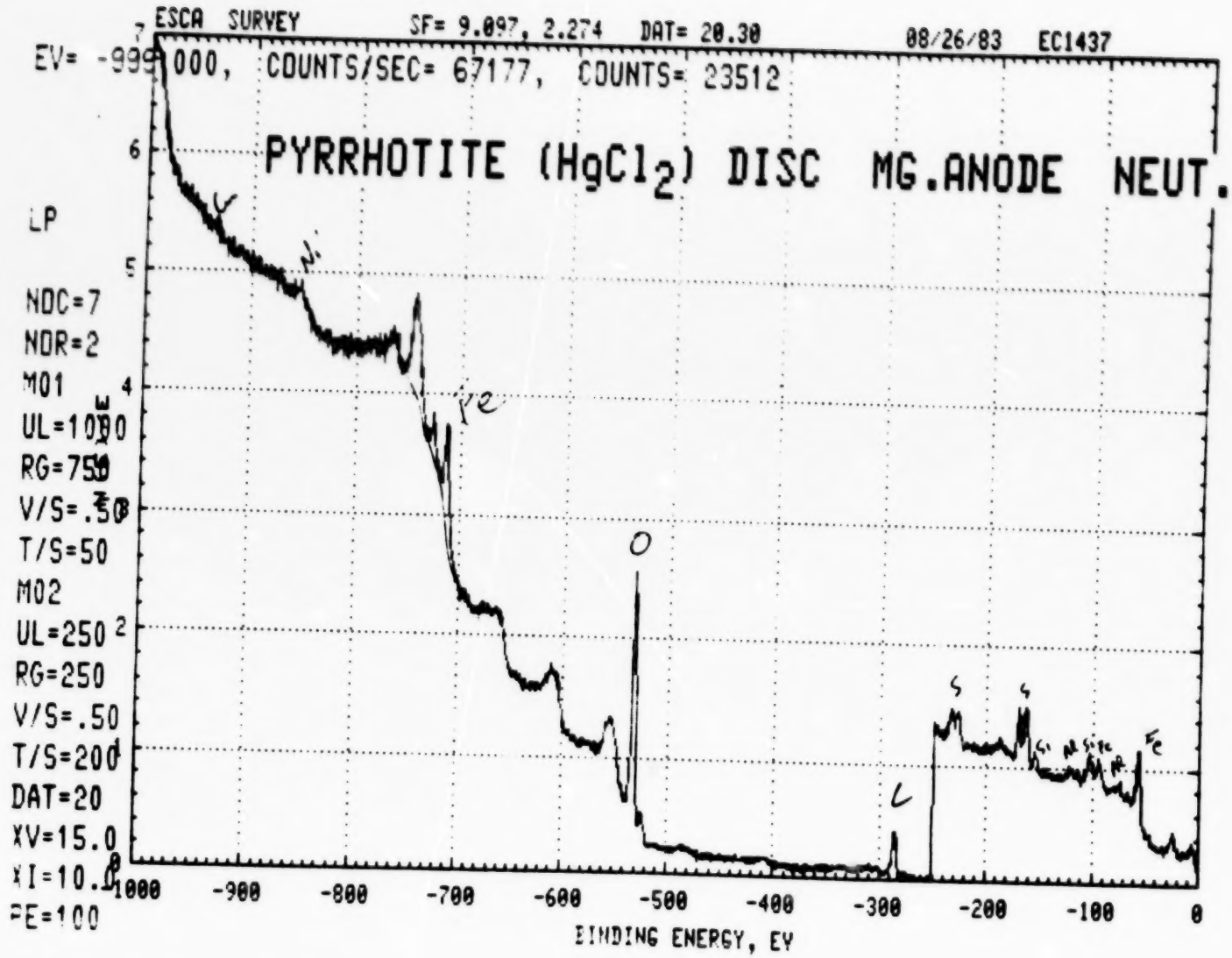
N(E)/E
BINDING ENERGY, EV
-250
-225
-200
-175
-150
-125
-100
-75
-50
-25
0
S
Zn
Si+Mg
Fe
O2s

Figure 5b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LP
NDC=7
NDR=2
M01
UL=1000
RG=750
V/S=.50
T/S=50
M02
UL=250
RG=250
V/S=.50
T/S=200
DAT=20
XV=15.0
XI=10.0
PE=100
7
6
5
4
3
2
1
0
V
Ni
Fe
O
L
S
S
Fe
-1000
-900
-800
-700
-600
-500
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-300
-200
-100
0
BINDING ENERGY, EV

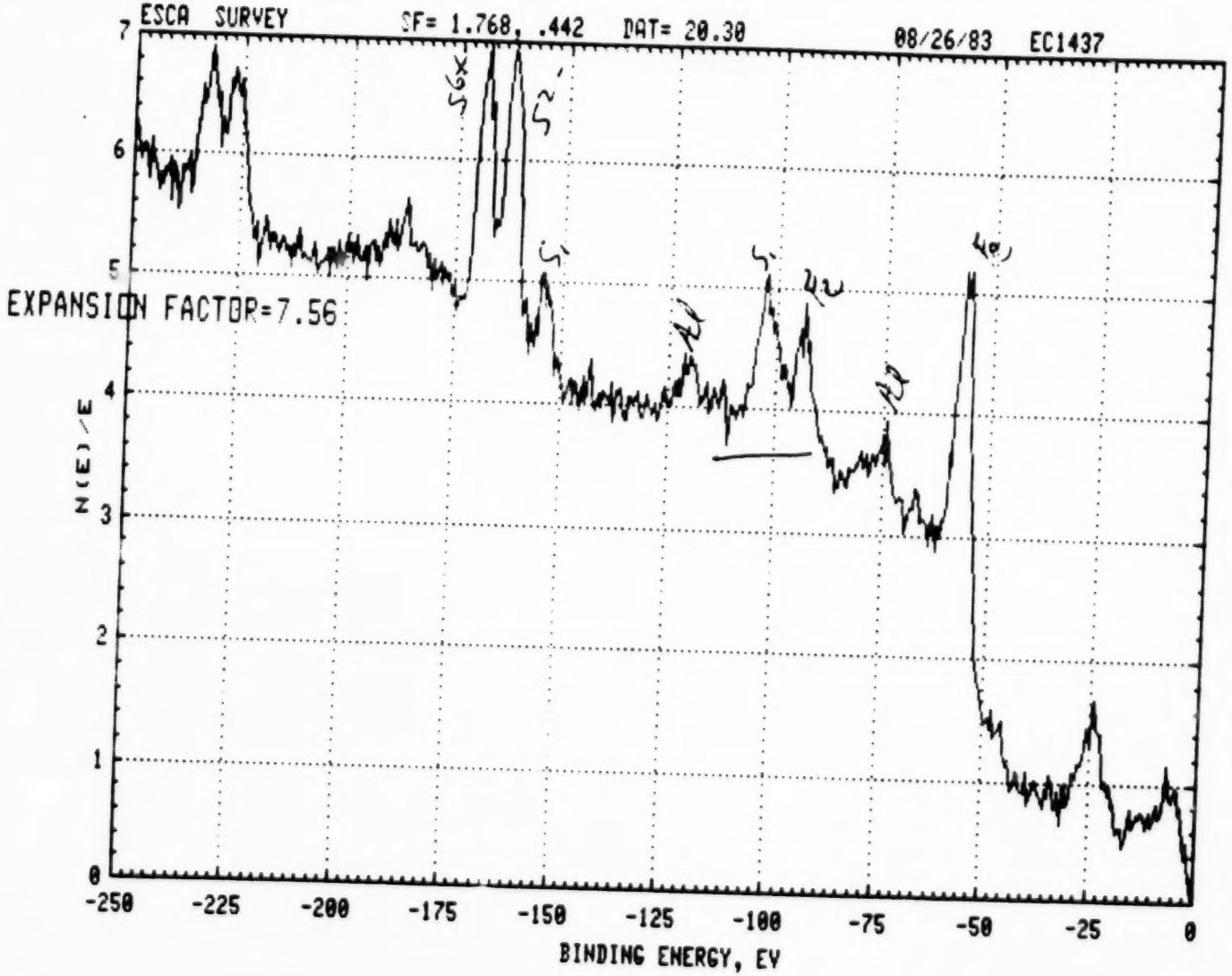
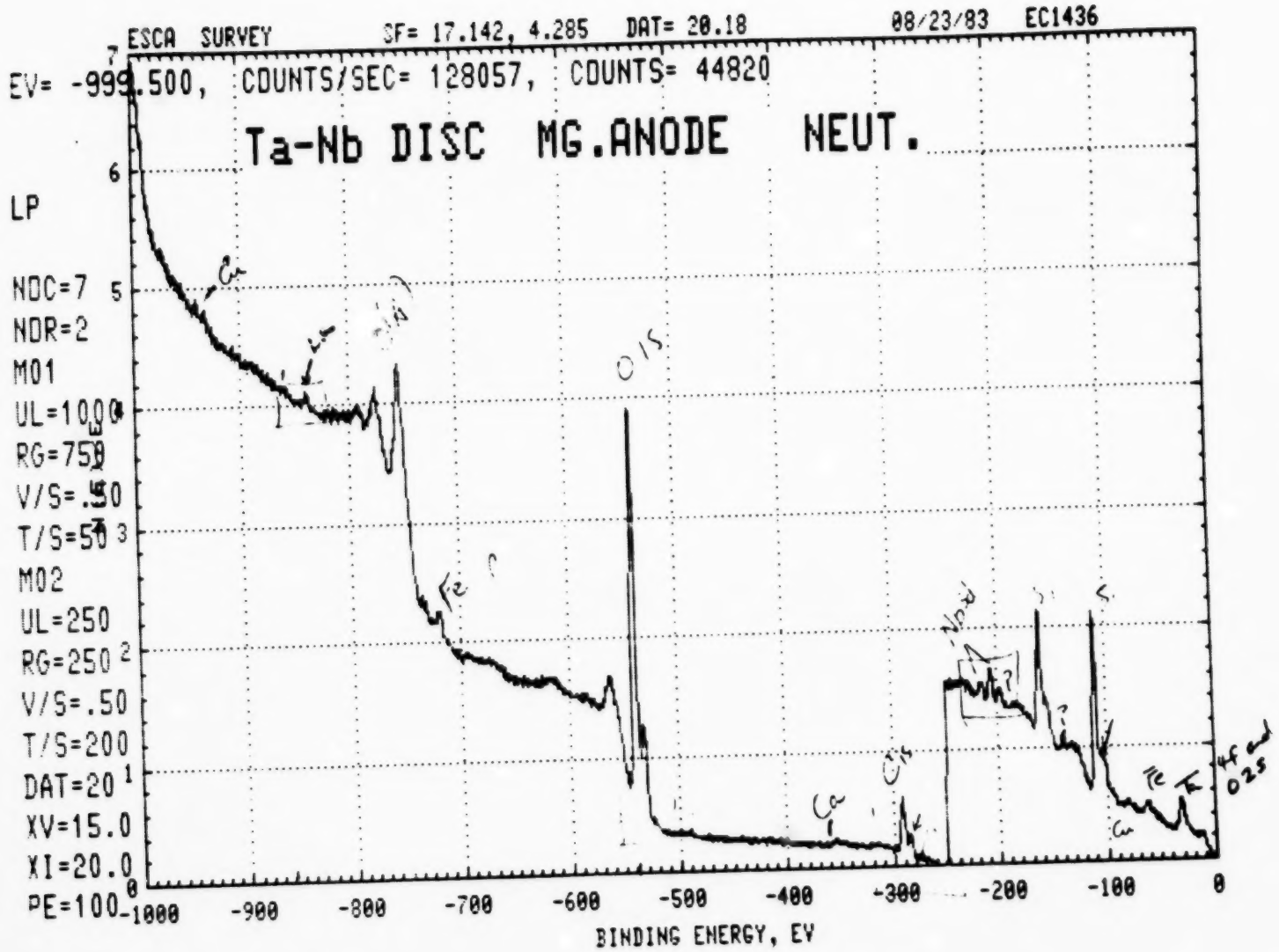

ESCA SURVEY
SF= 1.768, .442
DAT= 20.30
08/26/83
EC1437
EXPANSION FACTOR=7.56
N(E)/E
BINDING ENERGY, EV
7
6
5
4
3
2
1
0
-250
-225
-200
-175
-150
-125
-100
-75
-50
-25
0

Figure 6b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Ta-Nb DISC MG.ANODE NEUT.
LP
NOC=7
NOR=2
M01
UL=1000
RG=750
V/S=.50
T/S=50
M02
UL=250
RG=250
V/S=.50
T/S=200
DAT=20
XV=15.0
XI=20.0
PE=100
O 1S
Cu
Fe
Ru
Ta
4f and 02S
7
6
5
4
3
2
1
0
-1000
-900
-800
-700
-600
-500
-400
-300
-200
-100
0
BINDING ENERGY, EV

Figure 7a

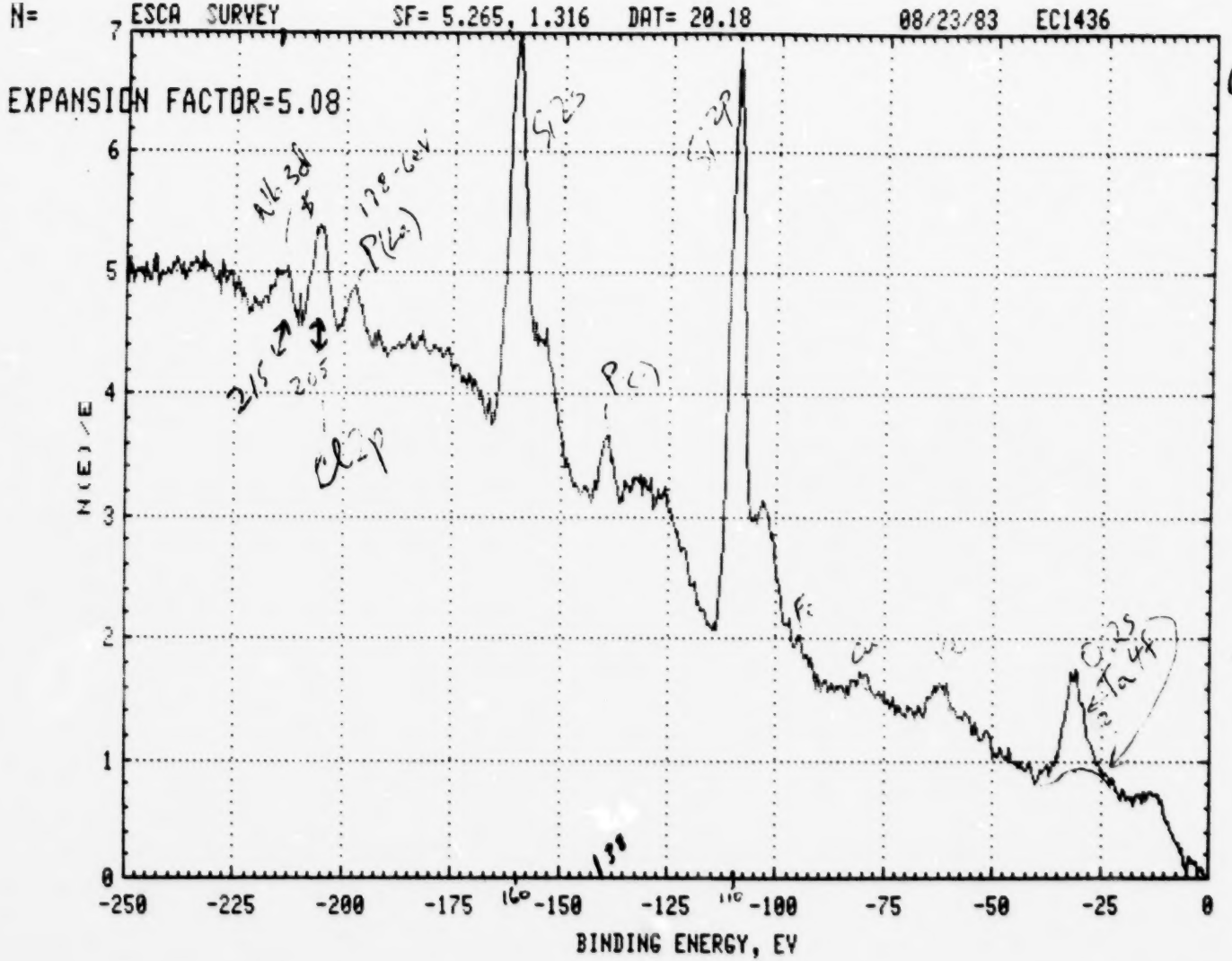

Figure 7b

Nb & Ta with P in alkaline (gneiss rocks)
also association with Ti, U, Th, rare earths
Pyrochlore

+7eV

POOR

QUALITY

ORIGINAL